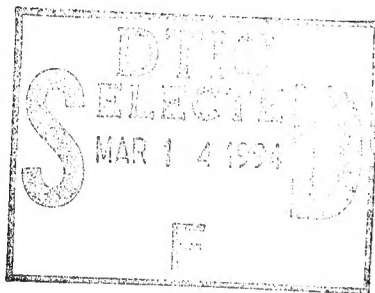


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Short Title of Work:

**Novel Photoelectric Sensing Technology for Environmental
Monitoring**

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Phase I Final Report

(A) Task Objective

We have proposed to develop and improve the function of a new environmental monitor using the Photoelectric Atmospheric Proportional Counter (PAPC) Sensor technology. This is a simple, reliable, inexpensive, hand-held instrument for chlorinated contaminant measurements. The proposed objectives are to review and assess relevant pollutant monitoring technologies, to conduct concept analysis and design of PAPC sensor, to carry out bench-scale experiments for investigating the key properties of PAPC for environmental monitoring, to analyze data and delineate development needs, and to document results.

(B) Technical Problems

A conventional proportional counter can be used only with a special counting gas such as P-10 (10% CH₄ and 90% Ar). Because the presence of oxygen molecules in air is likely to cause electron attachment to the oxygen molecules, it has been considered unlikely that a sensor with the principle of a proportional counter could be used to detect pollutants in the air. This is the major technical problem we would like to investigate and resolve.

The effects of foreign gases, such as NO_x, SO₂, gasoline, and water vapor, has to be investigated also. The bottleneck for broad applications of new chemical sensors is usually their lack of

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reversibility or reproducibility. A certain kind of chemicals or foreign gases may contaminate the sensor and the sensor may not recover to its original signal.

(C) General Methodology

Since chlorinated compounds usually have high electron affinity, the reduction of electron signals or the variation of electron drift-time can be used for detection of chlorinated contaminants. The amplification of electron signals can be achieved by using a PAPC technique. The unique character of this new sensor is that the chemicals selection (halogenated gas) and the signals amplification can be done at the same time.

In this project, our method of accomplishing the proposed objectives are as follows:

1. Sensing Technology Survey

By examine the literature on various monitoring concepts, we can define the applicability of the PAPC technology in terms of performance, sensitivity, service, cost effectiveness, competitiveness, and optimum means for producing desirable photoelectrons.

2. Concept Analysis

Based on the results of our survey, we can conduct conceptual analyses of how to design and build an experimental prototype which

hold excellent performance, sensitivity, service and still possess superior cost effectiveness and competitiveness.

3. Bench-Scale Tests

According to the design from our concept analysis, we can build a sensor experimental set-up. The works are to engineer and assemble hardware, to test various chemicals, and to investigate the factors affecting the sensitivity, stability, and reliability.

4. Evaluation and Reporting

The last step is to analyze the data obtained and evaluate the results generated from bench-scale tests. We will complete the documentation of our findings and recommendations in the final report, and develop a plan for the Phase II effort.

(D) Technical Results

We have designed, machined, and assembled a bench-top PAPC sensor. We have also tested this sensor with various potential pollutants listed in EPA. Optimum conditions have been found to achieve high sensitivity, stability, and reliability and also enjoy superior cost effectiveness and competitiveness.

The conventional proportional counters can be used to detect different kinds of radiation, and under suitable conditions, to measure radiation dose. A variety of gas mixtures, pressures, and tube shape are employed. The tube may be either of a sealed or gas-flow type. Such a counter utilizes a gas enclosed in a tube often

made with a fine wire anode running along the axis of a conducting cylindrical-shell cathode. When the potential difference is raised to a few hundred volts, the field strength near the anode increases to the point where electrons produced by the radiation (such as an alpha particle) and its secondary electrons acquire enough energy there to ionize additional gas atoms. Gas multiplication then occurs, and the number of ions collected in the pulse is proportional to the original number produced by the radiation and its secondaries. The tube can be used to measure the energy spectrum of individual alpha particles stopping in the gas. Gas multiplication factors of about 10^4 are typical.

In our design, we have adapted the hardware of proportional counter, but with a totally new concept. The configuration of experimental set up is shown in Figure 1a. The principle of our proportional counter is as following: a fixed amount of electron ion pairs are produced from the sensor's wall by light source (i.e. photoelectrons) outside the window , and then the acceleration of electrons near the counting wire creates an avalanche effect, which greatly amplifies ions pairs originating from radiation light source. If there is a trace halogenated-pollutant exists in the air, electrons will be grabbed by the pollutants, then a drastic decreasing of signal will occur. A photograph of our bench-top PAPC sensor is shown in Figure 1b (the length of the ruler in the photograph is 15 inches). The sensor body is a copper tubing with inner diameter of 5/8 inch. A layer of tin foil which furnishes photoelectrons is attached to the interior of the sensor by conducting paint. We used a 2 mil tungsten wire as the counting wire. One end of the wire was attached to a LiF

window and the other end was attached to a BNC electric feedthrough. The sensor body was sealed air-tight except two openings which were created for air-sampling purpose. The photoelectrons were produced by a flash-lamp (made by EG&G ELECTRO-OPTICS, Model PS 302) radiating to the surface of tin foil. At the same time, the flash lamp triggered the oscilloscope (Tektronix TDS 310, two channel oscilloscope) and data of electron-signals were taken for both amplitude and drift time. A high voltage of 2000 V was applied to the counting wire by a HV power supply (OXFORD TC 950A 5kV Bias Supply) and the signals from counting wire was amplified by a preamplifier (OXFORD TC 175, low noise preamp) before measured by the scope. A air pump was used to draw air sample from a air-sampling bag (Chemware Teflon FEP Gas Sampling Bags, for gas sample analysis). The flow speed was regulated by a flow meter (made by KOBOLD) and was set at 1.0 standard cubic foot per hour (SCFH).

We have tested this sensor with several pollutants and with various concentrations. The method we used for the preparation of gaseous phase standards is a modification of EPA Method TO-1. This method is recommended to all personnel in the Analytical Chemistry Division at Oak Ridge National Laboratory who wish to prepare organic vapor phase standards (Title: PROCEDURE FOR THE PREPARATION OF VAPOR PHASE STANDARDS USING THE STATIC DILUTION METHOD, Procedure No. AC-OP-300-0819). The air we used to dilute the pollutant standards was from a compressed air cylinder (supplied by Air Products, Ultrapure Carrier Grade Air). We have tested several chlorinated organic compounds which are listed

in EPA's publication (40 CFR, Lists of Pollutants and Applicability of Part 61, 7-1-93 Edition). These potential air pollutants include trichloroethylene (C_2HCl_3), chloroform ($CHCl_3$), trichloroethane ($C_2H_3Cl_3$), methylene chloride (dichloromethane, CH_2Cl_2), ethylene dichloride (1,2-dichloroethane, $C_2H_4Cl_2$), perchloroethylene (tetrachloroethylene, C_2Cl_4), and carbon tetrachloride (CCl_4). These chemicals and their short term exposure limit (STEL) standards regulated/recommended by OSHA/NIOSH are listed in TABLE 1. We can use two different methods to distinguish various concentration. One method is by measuring the amplitude change and another method is by measuring drift-time change. Since the oscilloscope shows both data at the same time, we recorded both of them and compared their sensitivities. The sensor detection capabilities on various chemicals are shown in Figure 2 through Figure 8. In each figure, the graph on the left shows the amplitude changes and the graph on the right shows the drift-time changes at various pollution concentrations (0.2 ppm to 200 ppm). From the above figures, we found that our sensor is capable of detecting the STEL limit for all the chemicals standards by OSHA/NIOSH. For most of the chemicals the detection limits of our sensor are two orders of magnitude lower than those required STEL limits. We have also tested our sensor with various concentrations (0.2 ppm to 200 ppm) of acetone (C_3H_6O). We did not observe any noticeable changes in this case.

TABLE 1. Potential air pollutants listed by EPA and current short term exposure limit (STEL) standards/recommendations by OSHA/NIOSH

| | OSHA Standards (STEL) | NIOSH Recommendation (STEL) |
|---|--------------------------|-----------------------------------|
| trichloroethylene (C_2HCl_3) | 100 ppm | |
| chloroform ($CHCl_3$) | 2 ppm | |
| trichloroethane ($C_2H_3Cl_3$) | 350 ppm | 350 ppm |
| methylene chloride (CH_2Cl_2) | 500 ppm | 100 ppm |
| ethylene dichloride ($C_2H_4Cl_2$) | 1 ppm | 1 ppm |
| perchloroethylene (C_2Cl_4) | 100 ppm | |
| carbon tetrachloride (CCl_4) | 50 ppm | 10 ppm |

(E) Important Findings and Conclusions

We have found that we can detect volatile chlorinated compound to a level as low as a few hundred ppb. We can quantify the pollutant concentration by either the signal's amplitude or the signal's drift-time. The selectivity of this sensor is as we expected that only halogenated gases can be efficiently detected. Other volatile organic chemicals (such as acetone) do not affect the sensor signals. This is a sensor with stability, sensitivity, and selectivity.

In this project, we have accomplished the bench-top system designed, engineering, and hardware assembly of the proposed sensor. We have systematically investigate its feasibility as a stand-alone monitor for various EPA pollutants in dry air.

(F) Implications for Future Research

We have found the following area need further research and development:

1. Laboratory Testing

We would like to obtain the information of sensor sensitivity vs. lamp power and sensitivity vs. voltage applied on the counting wire, so we can decide the minimum power needed to maintain a reasonable sensitivity. We would like to investigate the sensitivity and stability dependence on the material of counting wire and sensor's wall. A properly selected material should improve the sensitivity and save energy. The effects of various foreign gas (NO_x , SO_2 , gasoline, water vapor, etc.) will also need to be evaluated.

2. Product Design

We would like to miniaturize the sensor including packaging the electronics. Many parts of our experimental set up are stand alone commercial components (e.g. power supply). We should design our own components and integrate them into one simple device. After this, we will perform durability test and cost analysis.

3. Business Plane

After accomplished above tasks, we will be seeking manufacture company to produce the sensor. A marketing plan will also be prepared.

(G) Significant Hardware Development

The general task of a molecular or elemental analysis to identify chemical species in different environments is usually done by using the common analytical instruments, as listed in TABLE 2. So far the measurements of air pollutants have been carried out mostly by the use of analytical instruments based on optical spectroscopy or electrochemistry in the liquid phase. These instruments give precise analytical data, but in most cases they cannot monitor rapid changes in the concentrations of the chemical components in question, because they need long times for data acquisition, in addition to being expensive and bulky. Considering their market share in this survey, chemical sensors are still of minor importance, but their share is undoubtedly increasing steadily for well-known reasons such as their low cost, small size, microelectronics compatibilities, etc. Several features are compared between gas sensors and analytical instruments in TABLE 3. Gas sensors make it possible to detect air pollutants in real time. This feature is indispensable in their application for feedback control systems of various chemical processes. Compactness and low cost will also be advantageous, not only for application to mobile facilities but also for multi-site monitoring. The

development of gas sensors to detect various air pollutants is thus eagerly awaited.

TABLE 2. Most commonly used analytical instruments and estimated percentage of market share

| Analytical Instruments | Market Share (%) |
|--|------------------|
| High-performance liquid chromatographs | 23.30 |
| Gas chromatographs | 16.21 |
| Mass spectrometers | 12.40 |
| Liquid chromatographs | 7.81 |
| UV-visible spectrophotometers | 7.21 |
| Fourier-transform infrared spectrometers | 5.96 |
| Nuclear magnetic resonance spectrometers | 5.93 |
| Ion chromatographs | 4.05 |
| Thermal analyzers | 3.75 |
| Fluorescence spectrometers | 2.23 |
| Titration | 1.99 |
| Near-infrared spectrometers | 1.79 |
| Dispersive infrared spectrometers | 1.76 |
| Scintillation counters | 1.64 |
| Densitometers | 1.46 |
| Automated flow analyzers | 0.95 |
| Voltammeters | 0.72 |
| Raman spectrometers | 0.42 |
| Spectropolarimeters/ORD/CD | 0.42 |

TABLE 3. Comparison between analytical instruments and gas sensors

| | Analytical Instrument | Gas Sensor |
|-----------------------|---|---|
| Data Precision | excellent (absolute value) | excellent-fair |
| Data acquisition time | long | real time |
| Size | large | compact |
| Cost | high | low |
| Application | environmental monitoring stationary site | process control monitoring stationary site mobile site |

Rapid progress is being made in the development of sensors for CO₂, NO₂, NO, SO₂, ozone and fluorocarbons. Some of them, such as the CO₂ sensor, have almost reached a stage of practical application, while the rest of them are very promising. Most of these sensors have been fabricated with ceramic materials that are solid electrolytes and oxide semiconductors. The initiation of research and development on gas sensor for other miscellaneous pollutants, such as chlorinated compounds, is highly desirable.

We have developed a new environmental sensor using the Photoelectric Atmospheric Proportional Counter (PAPC) Sensor

technology. This is a completely different sensor technique compared with the most commonly used solid-state sensor technique. This sensor is able to select low level (a few hundred ppb) volatile-chlorinated-compound in the air. The estimated price of this sensor is below one thousand dollars. Currently, there is not such sensor (selectivity plus low price) available on the market.

(H) Special Comments

Currently on the sensor market, there are either very expensive (more than ten thousands dollars) high-selectivity sensors (such as FTIR) or relatively low price (about two thousand dollars) but non-selectivity sensors available. Our sensor is capable of selectively detecting halogenated vapor with a sensitivity two order of magnitude better than the OSHA's regulations (TABLE 4). If our sensor is commercialized, a variety of applications (such as health and safety, site characterization, clean-up process monitoring, environmental compliance, environmental modeling, and area modeling) can be used by industries and environmental-related companies. We believe our sensor (estimated price is below one thousand dollars) should be a high profit commercial product with a wide range of customer base.

References

Since our invention is relatively new, the only similar design is the refrigerant sensor by S. L. Allman et al. (reference 1). The

conventional proportional counter (for radiation detection) has a wide variety of designs in recent years, but the description of early work can be found in the book by J. Sharpe which is list in reference 2. The sensor surveys written by W. Gopel (reference 3) have been found very useful by the author in general chemical sensor research.

1. S. L. Allman, F. C. Chen, and C. H. Chen, "Charged Particle Mobility Refrigerant Analyzer," U.S. Patent #5,184,015, Feb. 1993.
2. J. Sharpe, "Nuclear Radiation Detectors, " New York: John Wiley & Sons, Inc. (1955).
3. W. Gopel, J. Hesse and J. N. Zemel (eds.), "Sensors: A Comprehensive Survey," Vols. 2 and 3, "Chemical and Biochemical Sensors," VCH, Weinheim, 1991 and 1992.

TABLE 4. Comparison between short term exposure limit (STEL) regulated by OSHA and sensitivity of our sensor

| | OSHA Standards (STEL) | Sensor Sensitivity (real time) |
|---|--------------------------|-----------------------------------|
| trichloroethylene (C_2HCl_3) | 100 ppm | < 0.2 ppm |
| chloroform ($CHCl_3$) | 2 ppm | < 0.2 ppm |
| trichloroethane ($C_2H_3Cl_3$) | 350 ppm | < 0.2 ppm |
| methylene chloride (CH_2Cl_2) | 500 ppm | < 2 ppm |
| ethylene dichloride ($C_2H_4Cl_2$) | 1 ppm | < 0.2 ppm |
| perchloroethylene (C_2Cl_4) | 100 ppm | < 0.2 ppm |
| carbon tetrachloride (CCl_4) | 50 ppm | < 0.2 ppm |

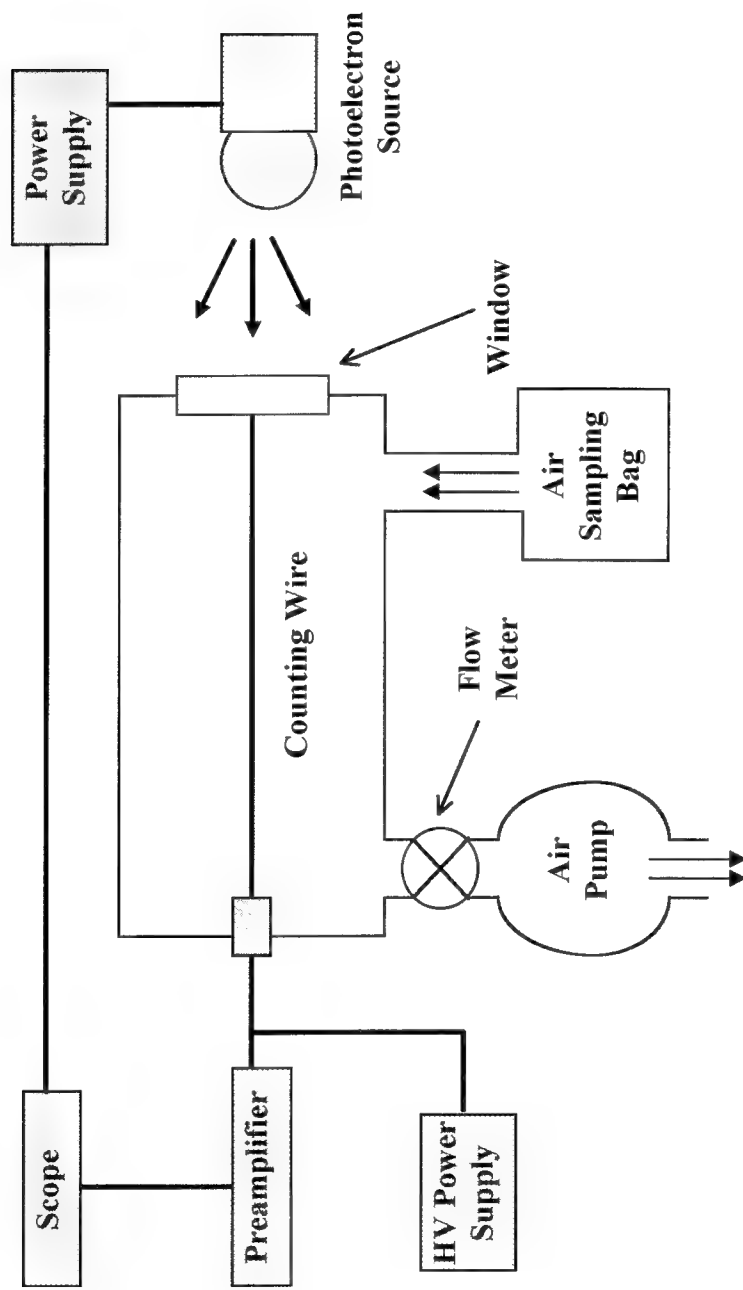


Figure 1a. Schematic of experimental prototype.

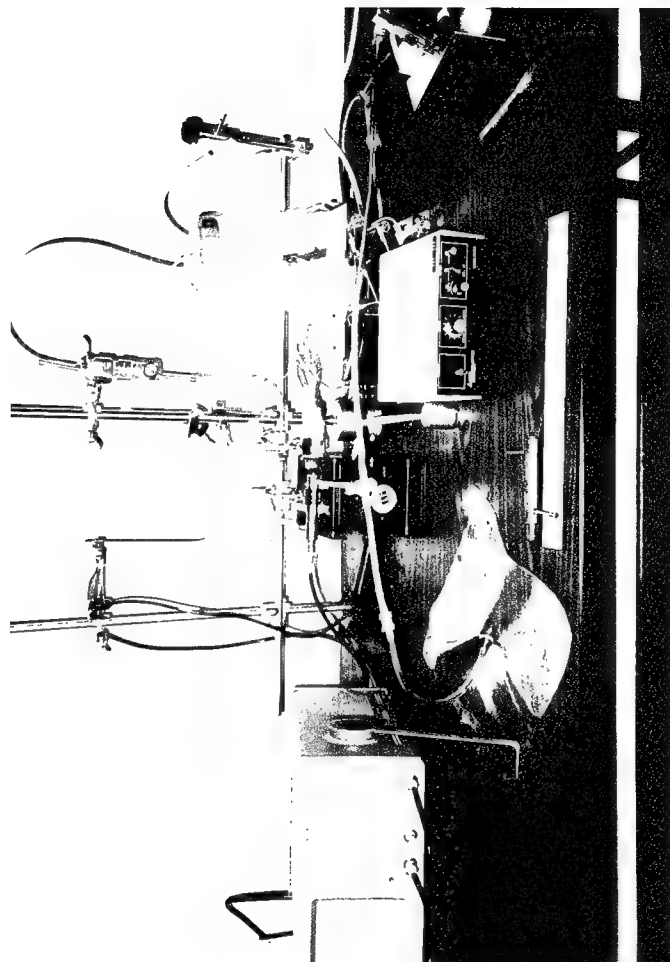


Figure 1b. Photograph of Experimental Setup.

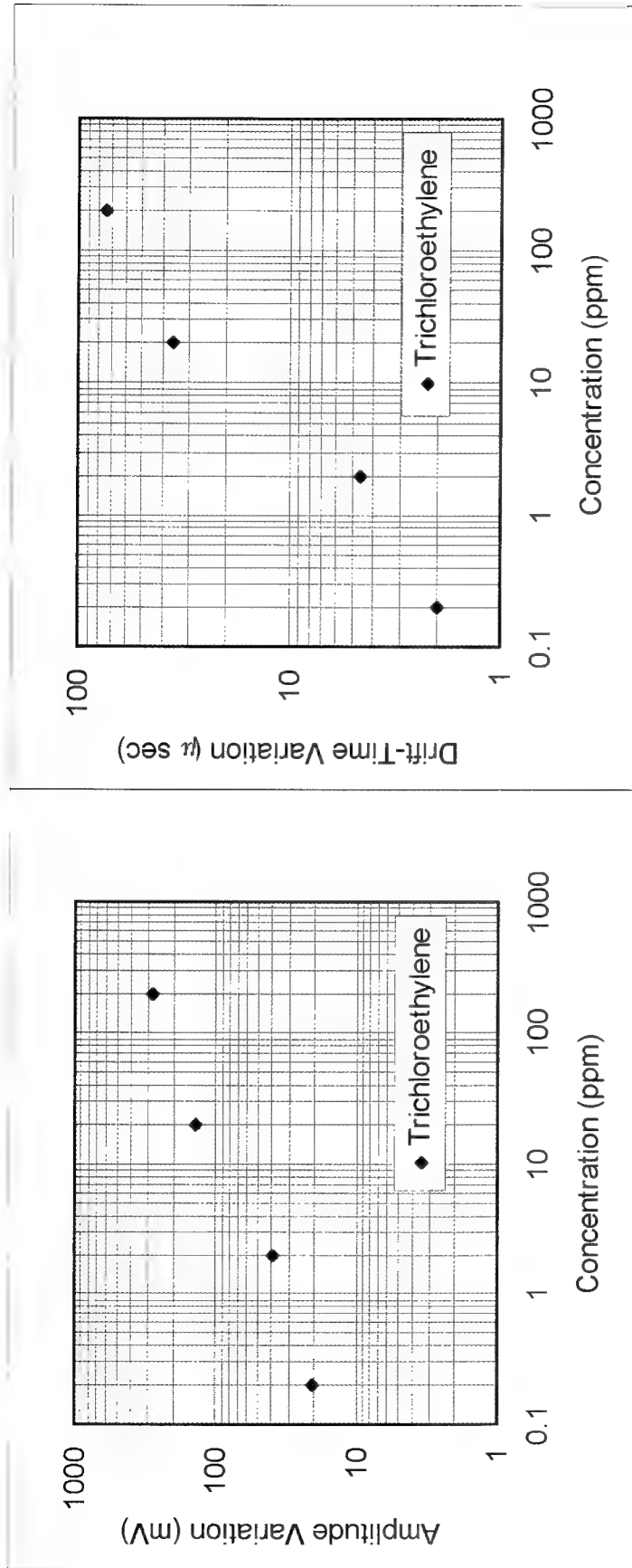


Figure 2. Amplitude and drift-time variations of trichloroethylene (C_2HCl_3)

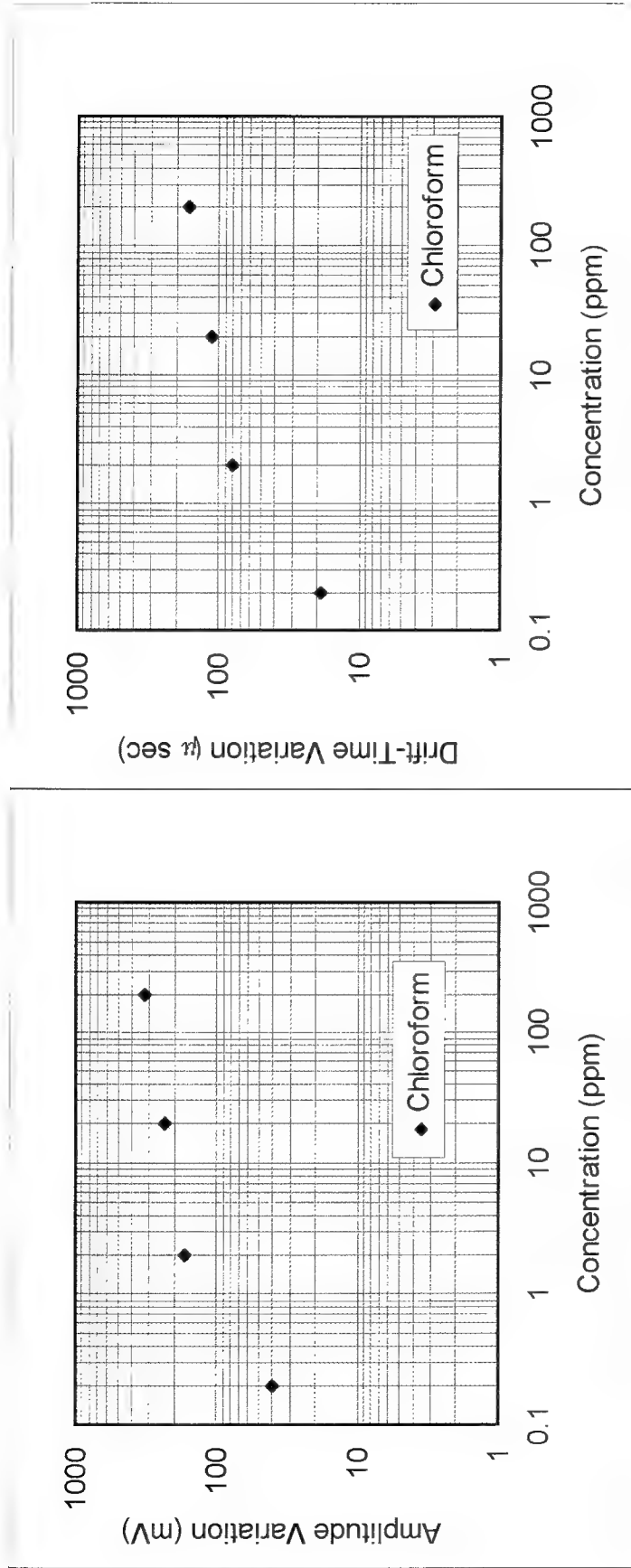


Figure 3. Amplitude and drift-time variations of chloroform (CHCl_3)

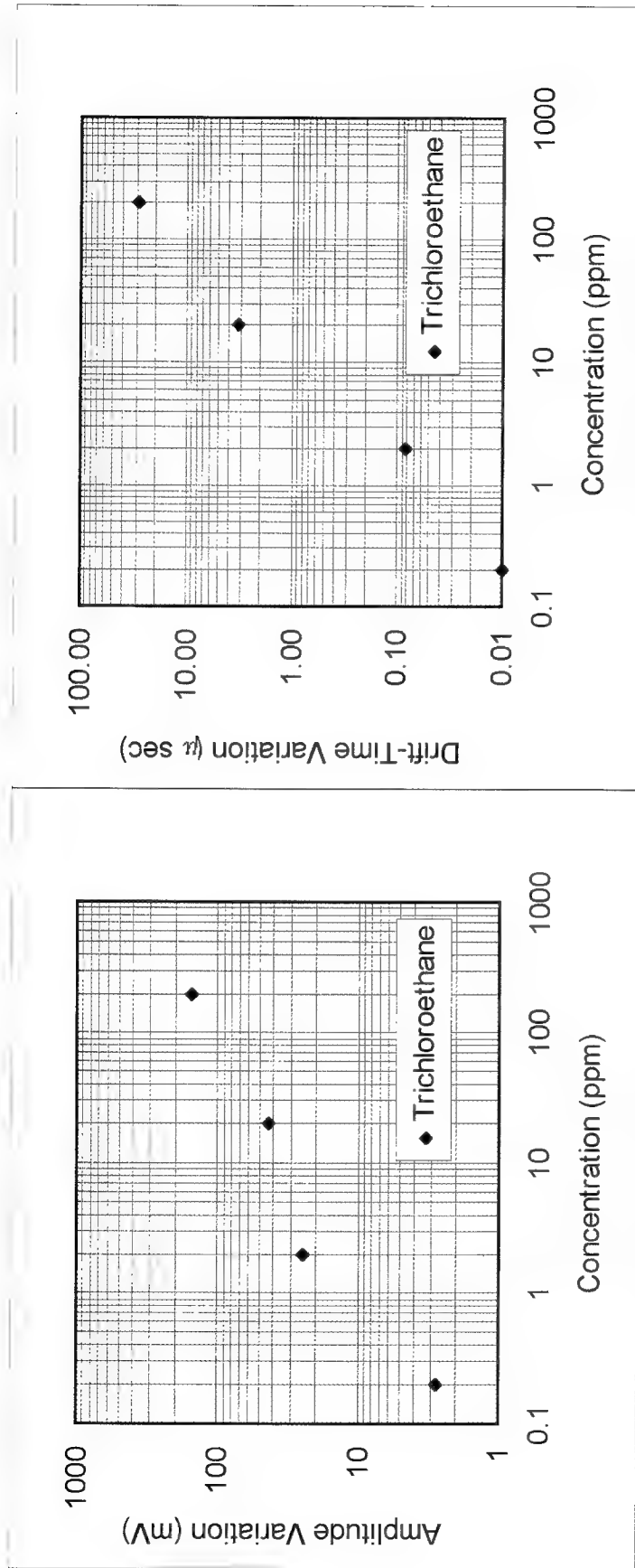


Figure 4. Amplitude and drift-time variations of 1,1,1, trichloroethane (CH_3Cl_3)

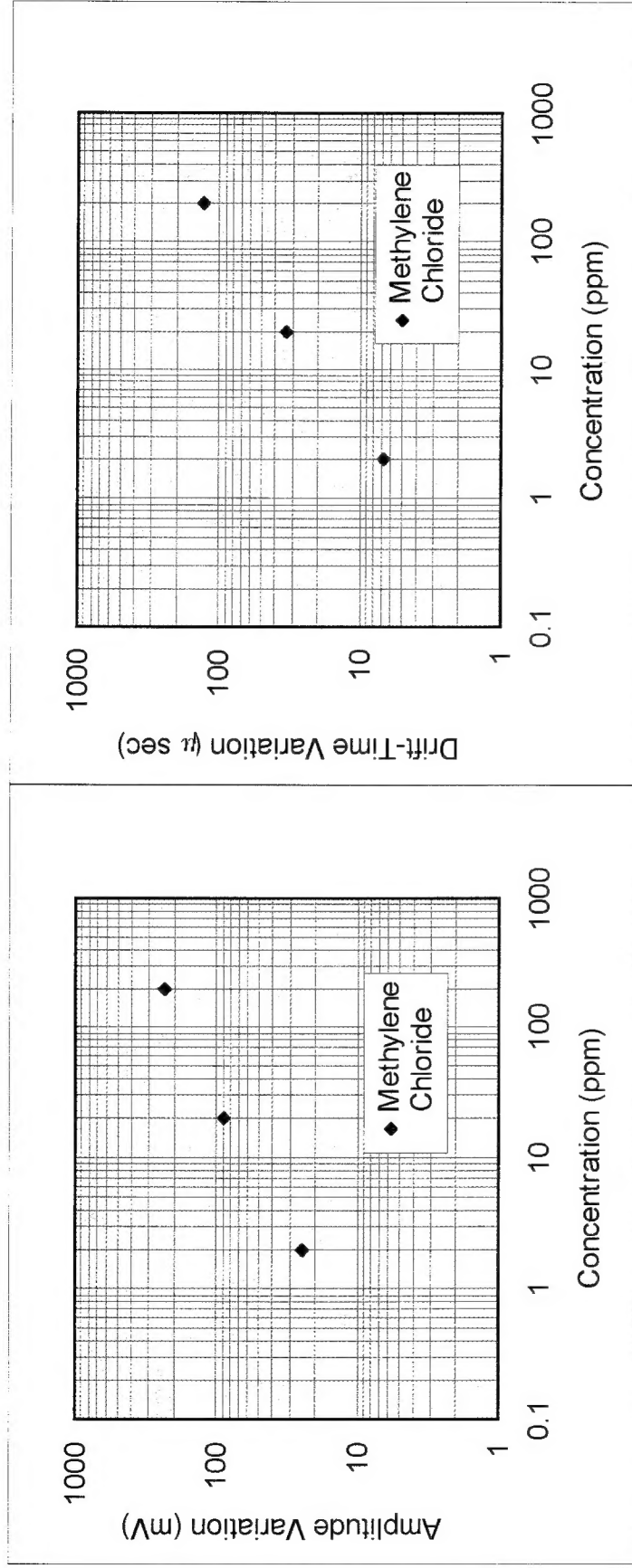


Figure 5. Amplitude and drift-time variations of methylene chloride (dichloromethane, CH_2Cl_2)

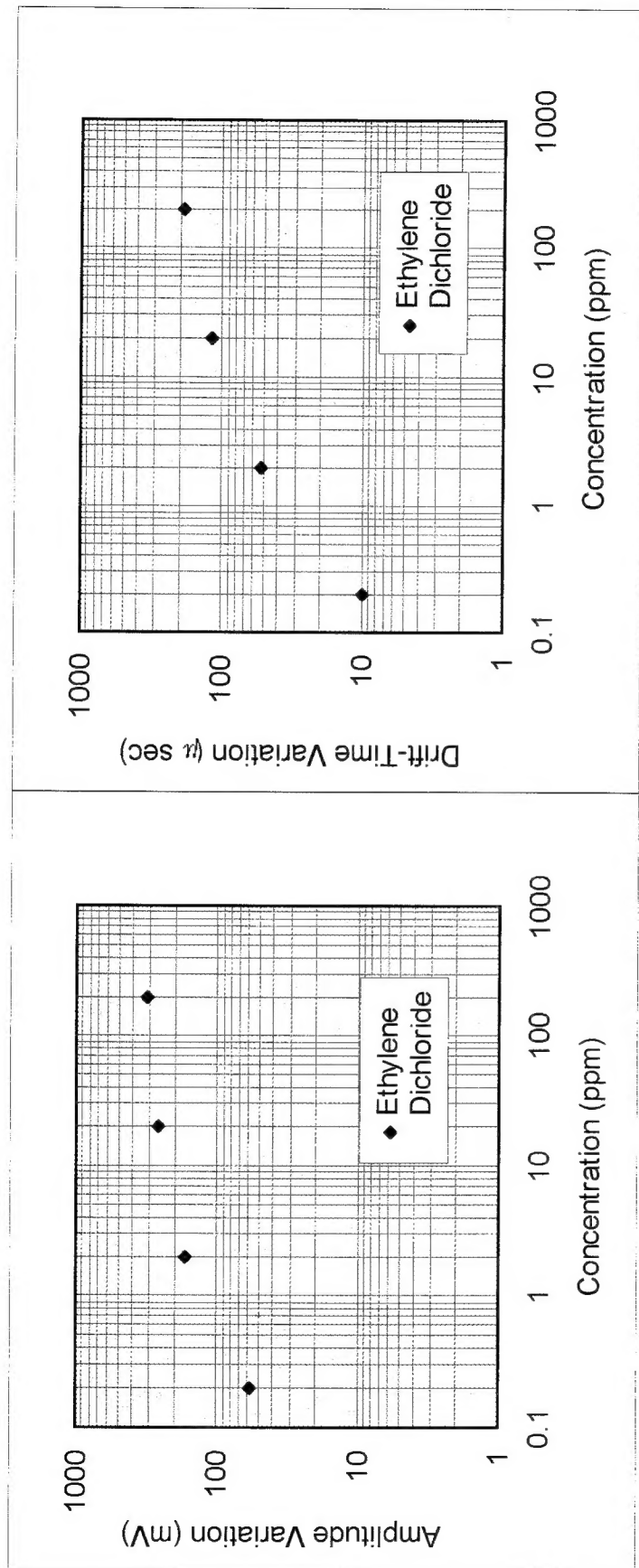


Figure 6. Amplitude and drift-time variations of ethylene dichloride (1,2 dichloroethane, $C_2H_4Cl_2$)

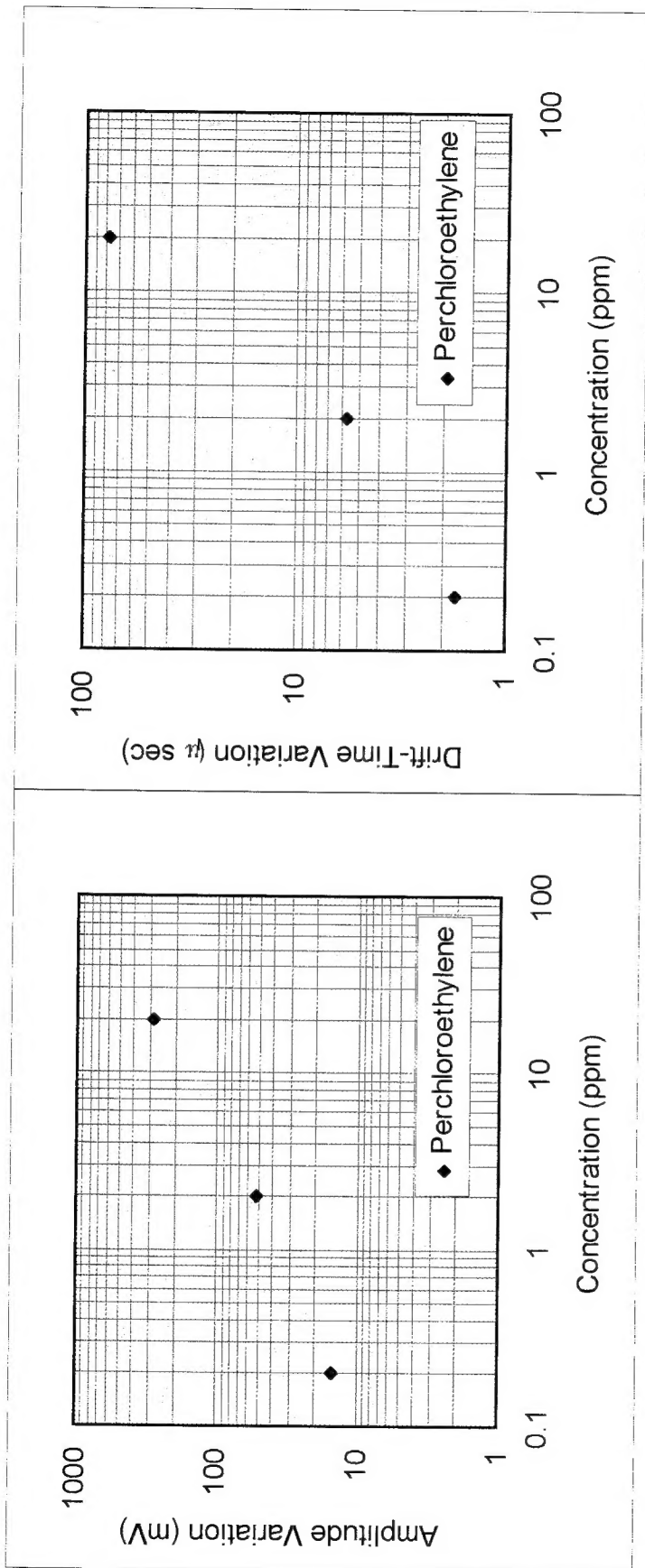


Figure 7. Amplitude and drift-time variations of perchloroethylene (C_2Cl_4)

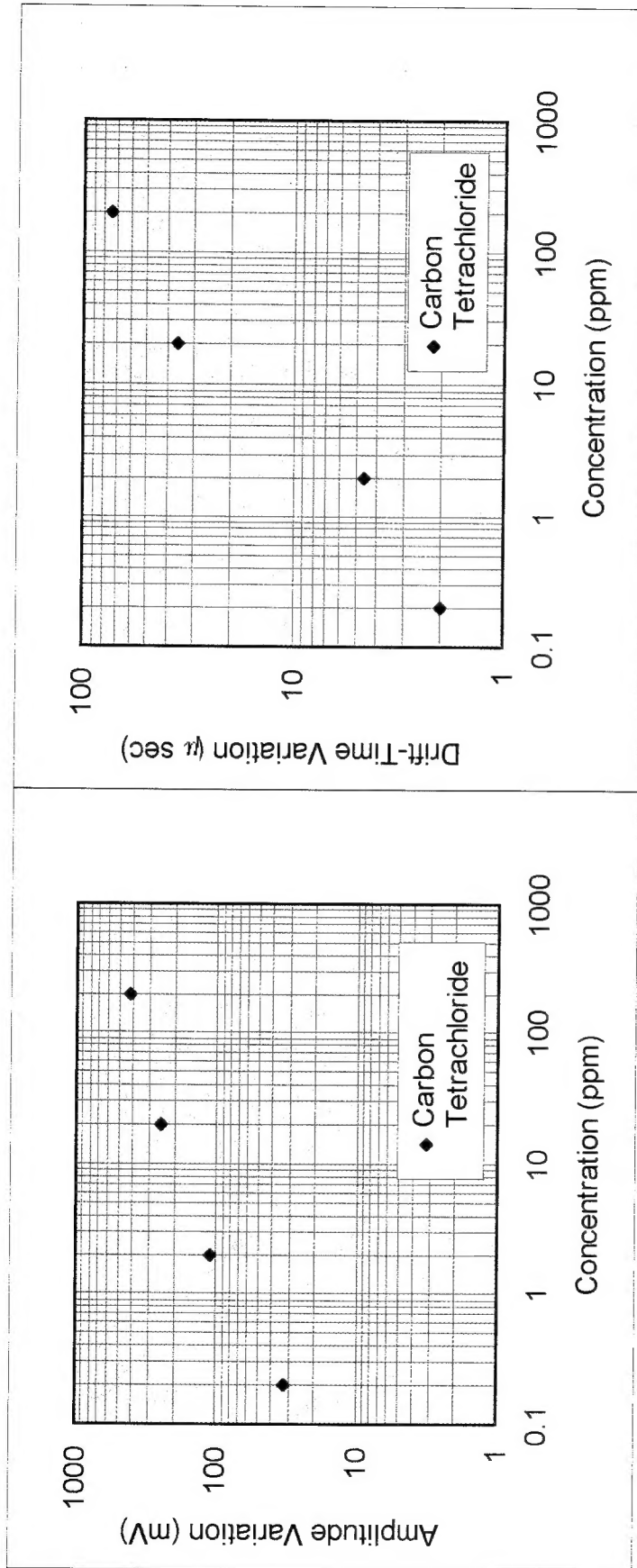


Figure 8. Amplitude and drift-time variations of carbon tetrachloride (CCl_4)